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FINAL REPORT

CENTER FOR SURFACE RADIATION DAMAGE STUDIES

AFOSR 90-0045

September 15, 1989 - November 30, 1992

Submitted by: Laurence D. Marks, Principle Investigator

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Executive Summary

Research focussed around understanding surface damage processes at the atomistic microstructure level was performed using high resolution electron microscopy in ultra-high vacuum and by other techniques. Techniques for obtaining clean and well-ordered surfaces and understand the images obtained have been developed and used to characterize damage processes. This data, combined with other high resolution electron microscopy data has been combined with analytical and numerical models with a high degree of success. Attempts to produce a small atomic oxygen source based upon electron stimulated desorption of oxygen neutrals led to the conclusion that literature estimates are much too high for the neutral to ion ratio. We have placed a strong upper bound on this ratio of < 10 , whereas values in the literature are as high as 10^7 .

Technical Report

1. Introduction

The overall objectives of the research were to improve our understanding of surface reactions and damage processes relevant to low earth orbit damage processes due to electrons, ions and atomic oxygen. To do this in a controlled scientific fashion, it was necessary to develop techniques for examining such processes for single crystals systems. Since many of the more important phenomena are related more to what happens to a material internally, rather than simply at the surface, subsurface penetration of damage is a very important process.

This general area was approached by a variety of different techniques. Our primary approach was to exploit electron microscopy under ultra-high vacuum (UHV) conditions. Electron microscopy has uniquely a very high spatial sensitivity to both the bulk and the surface, so is ideal for examining subsurface or near surface processes. Performing such studies requires clean, well-ordered starting materials, so a prerequisite to these studies was developing techniques for preparing these. It was also very important to improve the understanding of surface imaging using electron microscopes, which at the start of this work was at a relatively primitive level.

A second component of the work was to look at electron damage processes using a more conventional high resolutions electron microscope (HREM). Much of the exploratory work focussing upon transition metal oxides had been preformed as part of a previous grant. The focus here was more detailing the precise kinetics of the processes.

Synergistic with these experimental studies, theoretical work was also performed. One part of this was to attempt to model the phase transitions observed in transition metal oxides under irradiation. This has turned out to be very successful, with a general model that has been solved numerically as well as analyzed analytically. Some molecular dynamics simulations of the damage processes more at the atomic scale were also performed, with good

agreement achieved with experimental data for NiO.

Finally, we explored the development of a small atomic oxygen source. At the start of the project, the general literature stated quite clearly that neutral atomic oxygen of approximately the correct energy for simulations of low earth orbit conditions was readily available as a product of electron irradiation of certain oxides. Such a source would have been easy to incorporate into the UHV electron microscope. However, our initial attempts to check this as a preliminary to producing such a source failed. Continuing attempts to detect neutral oxygen desorption with higher and higher sensitivities also failed. The end result of this work is that we conclude that the general literature is incorrect, overestimating the neutral to ion ratio of oxygen desorption by factors of 10^5 - 10^2 .

2. Developments with UHV Electron Microscopy

At the start of this grant period, we had just started to be able to produce clean surfaces suitable for controlled surface science studies using gold. We have progressed enormously since then, and have learnt not only to handle simple materials such as gold but much more difficult ones such as the iridium and silicon (001) surfaces. These later surfaces are not simple to handle even with dedicated UHV chambers, and marrying the need to obtain very thin (10-100nm) samples along with clean ones is, we feel, an achievement.

Many of the details of how to do this have been published in the open literature, and in any case are relatively common sensical; all that is required is a high degree of care to cleanliness and control of the conditions of ion-beam cleaning and annealing of the surfaces. Although this sounds simple, when it has been attempted (to date) by other workers they have failed, and we suspect that it may still be some time before anyone else reproduces this for electron transparent samples.

Given high quality samples, it has become possible to obtain data whose quality has exceeded our own expectations. We will

mention here two very recent areas of progress where we have started to directly image surface structures and work out techniques for refining atomic positions to exceedingly high accuracies.

2.1 Quantitation of Surface Intensities

A key element of applying ultra-high vacuum electron microscopy has to be understanding the signal levels quantitatively; in any image the level to which the information can be understood depends critically upon the degree of understanding of the underlying theory. In principle the theory of transmission electron microscopy is very mature, but there has been little true quantitative analysis of the information.

In this grant period we have used electron energy loss spectroscopy to measure the absolute level of surface diffraction, discriminating between the true elastic diffraction and inelastic diffraction. The data obtained matches well to theoretically calculated values, providing additional confidence in the theory. In conjunction with experimental data obtained under NSF funding for the reconstructed iridium (001) surface, we have extended this further using x-ray R-factor fitting of the intensities obtained both from electron energy loss spectroscopy and from digitization of electron diffraction patterns. The results have been encouraging, although they have also demonstrated a need for better data collection procedures which are currently being developed as part of a separate ASSERT program funded by AFOSR.

Even further progress is currently taking place. We have very recently obtained similar (actually better quality) data for the Si (001) 2x1 reconstructed surface. At present, we appear to be able to refine the atomic positions of the atoms in this surface to accuracies of better than 2×10^{-2} Angstroms at a 68% confidence level.

2.2 Atomic Scale Imaging of Surfaces

A particularly dramatic result that has come out of research over the past year is that we have demonstrated, experimentally,

the feasibility of directly imaging atomic scale surfaces in the most general of all cases, namely when the electron beam is normal to the surface. Since 1983 it has been known that atomic scale images can be obtained using the so-called profile imaging technique, where the electron beam grazes the surface of interest. Unfortunately this technique is experimentally so limited that its use depends completely upon luck not experimental design or control. Experimental control is possible if the surface is normal to the electron beam, where there is the added advantage that atomic scale information about the bulk can be readily obtained.

It turned out, to our surprise, that this is simple to achieve; the scattering from a single monolayer is more than strong enough to be directly imaged in this geometry. One can either directly image using conventional HREM techniques, or tilt off the zone axis in order to attenuate the scattering from the bulk crystal.

The long-term implications of this result are substantial. It would appear to be routine to obtain atomic scale surface information with a resolution matching (or perhaps even better than) scanning tunneling microscopy for any material, plus direct information as to the atomic structure of the bulk. For instance, one should be able to directly correlate the atomic structure of bulk defects with the adjacent atomic surface structure without major problems.

3. Exploitation of the UHV Microscope

In the previous section we mentioned some of our achievements on the technical side of learning how to obtain information about surfaces using the instrument. Here we will sketch some of the data exploiting it more directly to look at surface damage processes.

3.1 Role of residual gases in electron damage phenomena

The majority of the work in this area was performed in the previous grant period. We were able to demonstrate quite clearly that many of the products of electron beam damage of oxides were very reactive, and their reactions with residual gases in the

background of a conventional microscope led to confusing results.

One system that we have studied in some detail is ReO_3 , which is a good test case since it should not damage via conventional mechanisms. However, it appeared to damage even in UHV conditions. Further investigation revealed that this was in fact due to a cross-reaction with carbon containing substrates. Properly clean ReO_3 on SiO substrates annealed in oxygen showed no damage. This reinforces our earlier conclusions.

We have also investigated the source of the surface spinel Ni_3O_4 that we observed in conventional microscopy by performing controlled atmosphere experiments. We have been able to rule out CO extraction of Ni as $\text{Ni}(\text{CO})_4$ by performing experiments in a controlled 10^{-7} torr atmosphere. In contrast, experiments in an oxygen atmosphere of 10^{-7} torr do show indications of the spinel formation, and this appears to be an example of electron beam oxidation producing a new metastable compound.

3.2 Laser damage of silicon

We have investigated the effects of laser irradiation on model Si (111) samples. The results have turned out to be fairly complicated. At low fluxes, cleavage was observed in thin film samples whereas at higher fluxes the whole 3mm sample was destroyed. What is particularly significant about our data is that the fluxes used are several orders of magnitude less than those found to cause damage in bulk silicon by other workers, and the temperatures at which this cleavage is occurring is much less. For instance, we have observed no evidence for surface melting and experimentally proved that there is no long-range diffusion of point defects on laser irradiation.

These results have all been explained semi-quantitatively in terms of thermal shock. Even though the temperatures are fairly low (500-600C) during the laser pulse, there is a reasonable temperature gradient across the samples of the order of 10-20C. The differences in the thermal expansion across the sample, which is at a low enough temperature that dislocations are immobile and

cannot readily relieve the stresses, will produce a shock wave and (we believe) cleavage.

3.3 Effects of Oxygen Plasma on Silver

It is known that atomic oxygen strongly attacks silver, and one commonly used source of atomic oxygen is an oxygen plasma. To probe this phenomena more closely, we have performed a series of experiments aimed at preparing a clean silver (110) surface and then exposing it to an oxygen plasma.

Sample preparation followed the techniques which we previously developed, namely ion-beam sputter cleaning and annealing. Although silver is sufficiently inert that this might appear simple, in fact it turned out to be exceedingly difficult to prepare a well-ordered surface. The problem turned out to be due to the fact that the temperature required to anneal out bulk defects (about 600-700C) is high enough that sublimation of the silver takes place leading to a rough surface.

The effect of the oxygen plasma also turned out to be somewhat of a surprise. We were expecting to see silver oxide, or possibly oxygen superstructures on the surface. Instead, the surface became atomically rough.

3.4 Other directions for UHV Electron Microscopy

Over the three year period of this grant we have also explored some new directions for UHV electron microscopy, some successful, other not. One of these for instance was an undergraduate project to explore gold deposition on germanium. Although the experiments were inconclusive, they pointed out to us a new direction which is currently being pursued as part of an ASSERT grant.

We have also performed some preliminary studies of the effect of oxygen on MoS₂ films in collaboration with Dr M. Hilton of the Aerospace Corporation. These have important applications as dry lubricants in the space environment, and oxygen and/or water vapor attack is a severe problem. Our preliminary data has indicated a strongly anisotropic oxidation process. At the present moment we are exploring possibilities of performing such experiments under

more controlled conditions

4. Non-UHV Electron Microscopy of Surface Damage Processes

The majority of the exploratory work using conventional high resolution electron microscopy was performed during the previous grant period. What we have been focussing more upon is details of the processes, in particular the kinetics. Three systems, NiO, WO₃ and V₂O₅ have all been studied. NiO and WO₃ are relatively simple and can be modelled (in a somewhat non-unique fashion) quite easily. The data for V₂O₅ was much more complicated, with multiple phase transitions and a strong electron beam dependence. This data has been successfully modelled theoretically as will be described below.

5. Theoretical Studies

5.1 Analytical Modelling of Surface Phase Transitions

We have been fortunate to have a visiting scientist (Dr Vitali Volpert) who is a mathematician specializing in numerical analysis of non-linear chemical reactions, a field very similar to the solid state phase transitions that we have found experimentally. He developed a numerical model for surface phase transitions due to the loss of oxygen from surfaces exposed to electrons or other sources of ionizing radiation. This is a fairly complete model at the continuum level, and includes as subsets of the model the more standard interface and diffusion controlled phase transition kinetics. Over the past year this has been generalized to a more complete analytical model of the same phenomena, extended to include more complicated interfacial reaction kinetics.

The main conclusions of this work are:

- 1) A very wide range of apparently different experiments kinetics can all be modelled with few floating parameters provided that the effective diffusion constant and the oxygen loss rate from the surface are both electron beam flux dependent. Fairly good agreement between numerical models and the experimental data was obtained. This result explains apparently contradictory data in the literature as consequences of different kinetic conditions.

2) We have been able to prove, analytically, that the propagation of multiple phase fronts observed experimentally in vanadium pentoxide with the disappearance of certain phases can only be understood with a model based upon mixed interfacial and diffusion control; conventional simplified models cannot explain this result.

3) The analysis indicated that the phase front propagation was stable to perturbations (e.g. dendritic growth should not occur), but need not lead to completely flat interfaces. This correlates well with the experimental observation of some interfacial roughness.

4) Depending upon the kinetics of the interfacial reactions, multiple modes of propagation were found to exist. Such phenomena are known in gas phase reactions, but to our knowledge this is the first prediction of them in the solid state. Transitions from one mode of propagation to another correlate with changes in the kinetics both during initial "incubation" periods and with the electron beam flux.

5.2 Molecular Dynamics Studies

The dynamics of the production of radiation damage in NiO were studied employing molecular dynamics in microcrystals ranging in size from 3,456 to 19,200 ions. The time evolution of a microcrystal was followed numerically by integrating Newton's equations of motion of all the ions. A fifth-order predictor-corrector algorithm -- Gear's algorithm -- was employed, and the simulations performed using a microcanonical ensemble. As is the case for most oxides NiO was treated employing an ionic scheme; specifically we employed a rigid-ion potential recently developed by Massobrio and Meyer, which provides a reasonable quantitative representation of real crystal properties, such as the cohesive energy and the elastic constants. In our code, the Ewald summation technique was used to calculate the Coulombic contribution to the potential energy and the forces. The model system -- NiO -- has the simple rock salt (NaCl) crystal structure. Three dimensional periodic boundary conditions were employed, with initially, all of

the ions were at rest on the sites of a perfect lattice. A radiation damage event was initiated by suddenly transferring momentum to an ion of the microcrystal -- this ion is called the primary knock-on ion (PKI) -- from an incident particle. In the present work, we focus our attention on PKI's with an energy of <150 eV, as we study the production of the primary state of damage at or slightly above the threshold energy for producing stable radiation damage. The anion or cation chosen to simulate the PKI was given an additional momentum along different crystallographic directions. After the PKI event the system was allowed to continue its trajectory in phase space. The evolution of the cascade of displacement or replacement events was followed during a time interval sufficiently long for all the interesting physical events to occur.

In the present study, the angular dependency of energy propagation of the knock-on events was studied via energy correlation diagrams in the {001} and {110} planes. Along the <110>-type directions, which is the most efficient direction to transfer the energy from the knock-on ion, investigation of the energy loss process was carried out in detail. In addition, the number of replacement ions as a function of the PKI energy was obtained for the <110>-type directions.

The main conclusions of the present molecular dynamics simulation study are as follows:

1. Assisted focusing along <110>-type directions was shown to be predominant via 80 eV energy correlation diagrams for both Ni and O PKI's in the {001} and {110} planes in NiO. Focusing along <100> directions was also shown to be significant, whereas for all other directions in the {001} and {110} planes the propagation of radiation damage was almost isotropic.

2. By analyzing the energy correlation diagrams and comparing our results for NiO with earlier results for KCl and NaCl, we find that mass mismatch affects the propagation of replacement collisions sequences more than the mismatch of the atomic radii of the cations and anions.

3. The rate of energy loss was approximately constant for an 80 eV O^{2-} PKI along the $\langle 110 \rangle$ -type directions. The rate of energy loss for an 80 eV Ni^{2+} PKI along the $\langle 110 \rangle$ -type directions exhibited a logarithmic behavior that shows a more rapid decrease than the linear behavior of the 80 eV O^{2-} PKI along the $\langle 110 \rangle$ -type directions.

4. The number of replaced ions along the $\langle 110 \rangle$ -type directions was found to be linearly dependent on the PKI energy and its first derivative with respect to the knock-on energy was almost reciprocally proportional to the ionic mass in the energy range of $E_d \leq E \leq 3E_d$, where E_d is the displacement threshold energy for the $\langle 110 \rangle$ -type direction. The number of displaced ions was a constant within the energy range studied in the present work for a primary knock-on event along the $\langle 110 \rangle$ -direction.

6. Neutral or Ionic Desorption from Surfaces?

The reactivity of the low earth orbit (LEO) environment is the motivation for the research described in this section. The principal reactive component of the LEO 200 to 600 km altitude is atomic oxygen. At an orbital velocity of 8 km/s, an "orbital wind" generates fluxes of 10^{13} - 10^{15} atoms/cm²-s with a collision energy of 5 eV. This reactive environment causes a number of materials degradation problems for orbiting space vehicles.

The initial objective of this research was to elucidate the kinetics and mechanisms of surface reactions produced by energetic atomic oxygen to provide a scientific basis for developing materials resistant to the LEO environment. The atomic oxygen beam required to simulate the LEO environment in the laboratory was to be generated by the electron stimulated desorption (ESD) of oxygen from transition metal oxide targets. The available experimental evidence strongly suggested that the ESD process was an excellent candidate for the abundant production of energetic atomic oxygen. Electron beam induced reduction of oxide surfaces and direct observation of oxygen ions emitted from the surface having the appropriate kinetic energy are established facts. The expectation

that neutral desorption dominates ionic desorption has been stated repeatedly in the ESD literature. Moreover, the detection of ESD generated O-atoms with a neutral to ion ratio, $O/O^+ = 10^7$ has been reported from a silver target charged with oxygen,¹ and plans to develop an ESD O-atom source based on this material system have been described.²

Unfortunately, the ESD O-atom source was never realized. Despite extensive efforts involving three different experimental approaches we were unable to verify the claims of large O/O^+ ratios from any of a number of metal oxide systems (O/Ag, O/Ta, O/Ti, O/W, and O/V) prepared using a variety of procedures (flame oxidation, UHV oxygen dosing, 1 atm O_2 exposure). As a result of this situation the focus of the research was redirected to provide a critical assessment of the O/O^+ ratio obtained from the O/Ag system which had been previously reported to have a value of 10^7 . While a number of experiments were performed on this system this final report will describe only the most definitive experiment.

The general approach to the experimental investigation of oxygen ESD is depicted in Fig. 1. A beam of electrons is fired at the ESD target and the desorption is detected with a mass spectrometer. A wire mesh is employed to repel O^+ ions produced by ESD. The transmitted neutral O-atoms are ionized, mass selected and detected in the mass spectrometer. The specific experiment employed here is diagrammed in Fig. 2. The ESD target is positioned at the entrance, A1, of a linear time-of-flight mass spectrometer (TOFMS). A pulsed electron beam is directed on the target to produce a pulse of ESD species. By adjusting the potential between the target and A1 all ESD species (neutrals+ions) or only neutrals are injected into the TOFMS. ESD ions are accelerated by a potential established between A1 and A2, focused by an electrostatic lens created by A2 and A3, and then drift along a 1 meter field-free tube to a detector where their arrival time is recorded.

Neutral oxygen atoms are photoionized using resonance enhanced

multiphoton ionization (REMPI). The output of an excimer pumped tunable dye laser is frequency doubled by a beta barium oxide doubling crystal to provide intense pulse of ultraviolet radiation in the vicinity of 226 nm. By tuning the ultraviolet radiation oxygen atoms are ionized by a resonant 2+1 excitation process via the 3p state as diagrammed in Fig. 3. This is a very efficient process; essentially all of the oxygen atoms in the focal volume of the laser are ionized. The electron beam and the ionization laser are pulsed according to a well defined timing program, and the detected ion signals are averaged over many pulses to obtain good statistics.

The ESD target was prepared by flame oxidation of 0.25 mm thick silver foil. The sample was supported by tantalum wires and positioned by a commercial X-Y-Z manipulator. The target was heated radiatively by a tantalum wire positioned behind it. During a typical experiment the sample was held at 200°C to promote replenishment of surface oxygen by diffusion from the bulk.

A calibration of the O-atom REMPI spectrum was obtained using gas phase NO_2 . NO_2 is efficiently photodissociated in the 226 nm region to produce NO and O by the same laser pulse which ionizes the atomic oxygen. The REMPI spectrum of atomic oxygen was recorded as a function of wavelength and is shown in Fig. 4.

With suppression of ESD ion emission, the presence of neutral oxygen atom ESD was probed using the REMPI technique. A typical result of this experiment is shown in Fig. 5. Trace a is the TOF spectrum obtained by photodissociation/photoionization of gas phase NO_2 . Signals corresponding to NO^+ and O^+ are clearly present. Trace b corresponds to the ESD experiment. While some NO^+ signal from MPI of residual NO in the apparatus is evident, no O^+ is detectable. A number of experiments were performed to investigate various time delays between the ESD electron beam pulse and the ionizing laser pulse. Experiments were performed at various target temperatures and degrees of surface oxidation. Measurements on gas phase NO_2 were performed repeatedly before and after ESD

experiments to guard against drift in the ionizing laser wavelength. Under no circumstances were any neutral oxygen atoms detected.

In the absence of a detectable neutral oxygen ESD signal we have employed the standard IUPAC convention to determine a detection threshold for the O-atom flux from the surface. If we assume a kinetic energy for O-atoms of 5 eV and employ our measurements of NO₂ to obtain the minimum detectable density of O-atoms in the laser focal volume and account for the solid angle subtended by the focal volume above the surface, the minimum detectable flux of O-atoms leaving the surface is calculated to be $5 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$. The measured O⁺ flux under identical experimental conditions was found to be $4.2 \times 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$ which results in a maximum O/O⁺ ratio of 8.5.

At the this time the reasons for a discrepancy between previous reports of an O/O⁺ ratio near 10^7 and the present results are not clear. What is clear is that the discrepancy cannot be due to our inability to detect atomic oxygen that was in fact produced by ESD of the O/Ag system. Though it has been widely stated that neutral desorption is generally the majority process in ESD, it appears that no reports have been made of the ratio of neutrals to ions based on direct measurements of both species. Indirect measurements have been presented. In such experiments, an ESD ion flux is measured and the neutral desorption yield is inferred from the ion yield decay as a function of time or post electron irradiation surface analysis of the target. The ratios of neutrals to ions determined in this manner tend to fall in the 10 to 1000 range.³ These results have been universally accepted and are the basis of the conventional wisdom in the ESD field.⁴ Clearly the results of this study fall within the expected range of neutral/ion ratios, albeit at the lower end, whereas the results of previous work on the O/Ag system are several orders of magnitude outside of this range.

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3. M. Nishijima and F. M. Propst, Phys. Rev. B2, 2368 (1970).
4. P. Fuelner, in Desorption Induced by Electronic Transitions (DIET II), ed. W. Brenig and D. Menzel, (Springer, Berlin, 1985), p. 142.

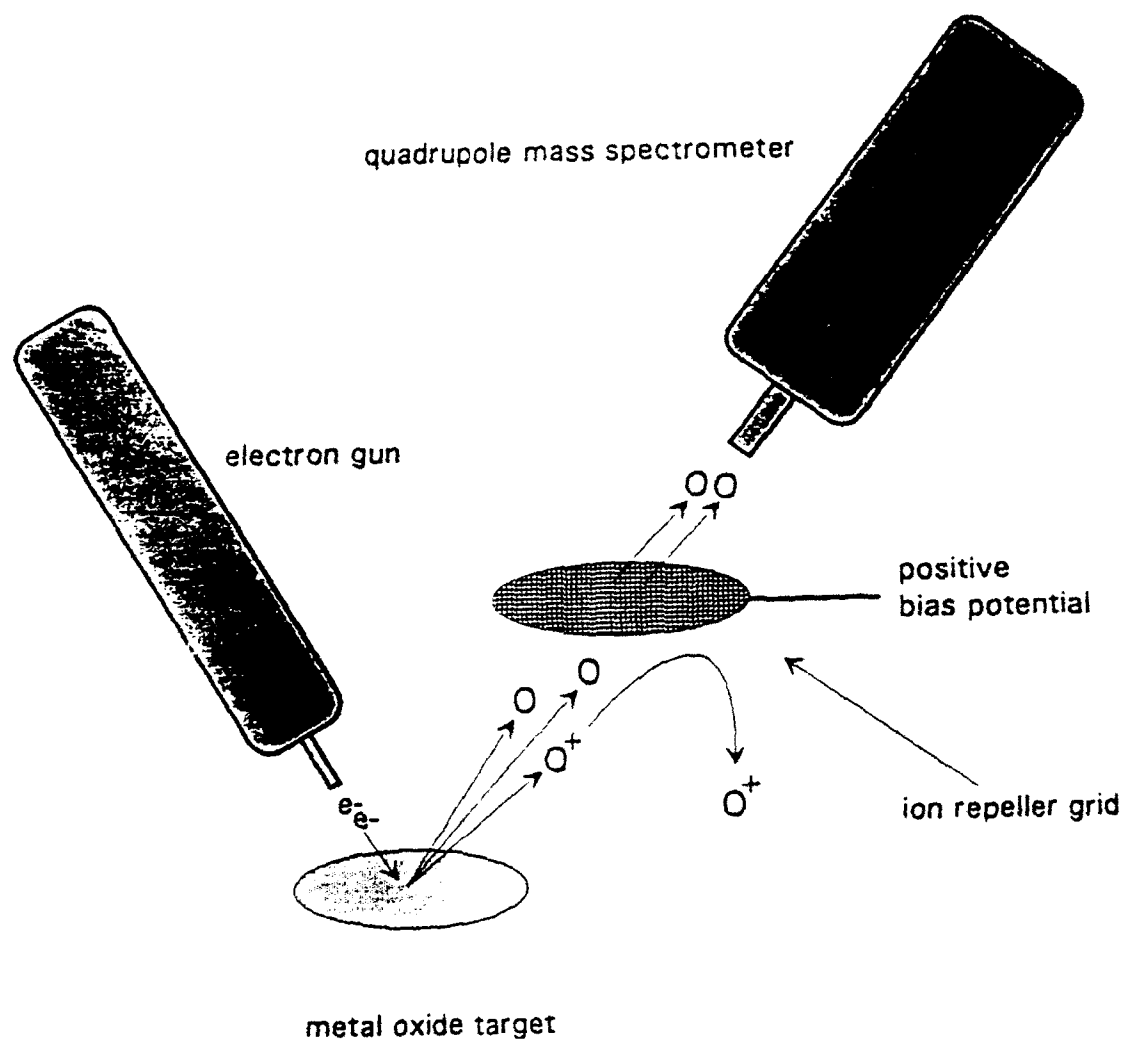


Figure 1 Experimental apparatus for the QMS detection of ESD generated atomic oxygen.

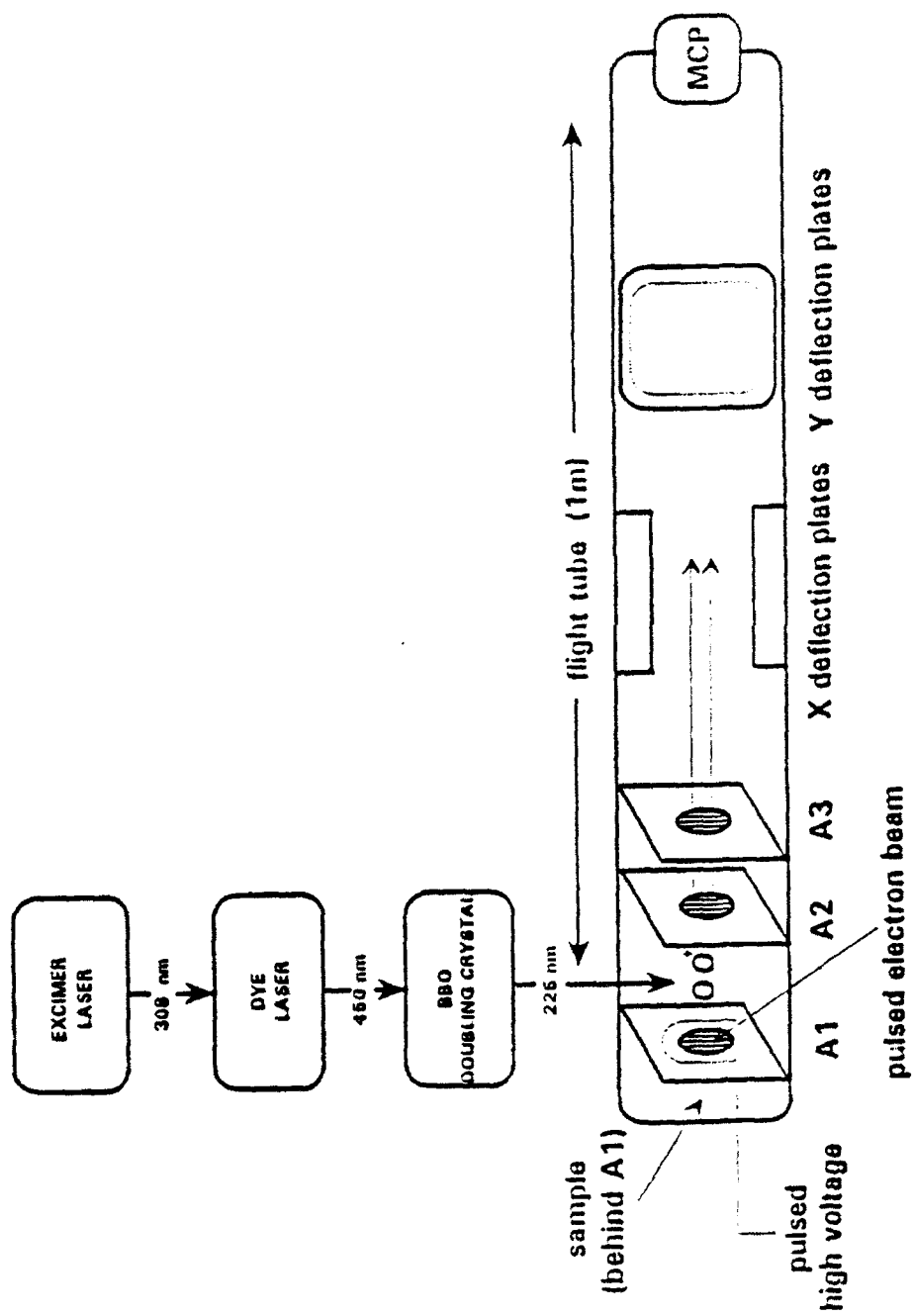


Figure 2 Experimental apparatus for the multiphoton ionization and time-of-flight detection of ESD generated atomic oxygen.

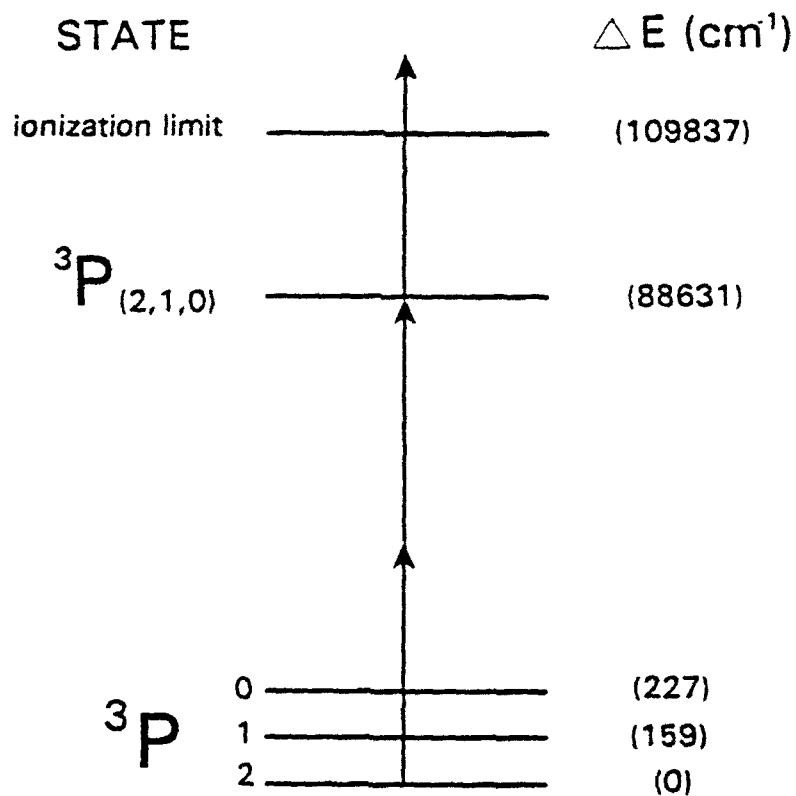


Figure 3 Energy level diagram for the 2 + 1 resonance enhanced multiphoton ionization of atomic oxygen.

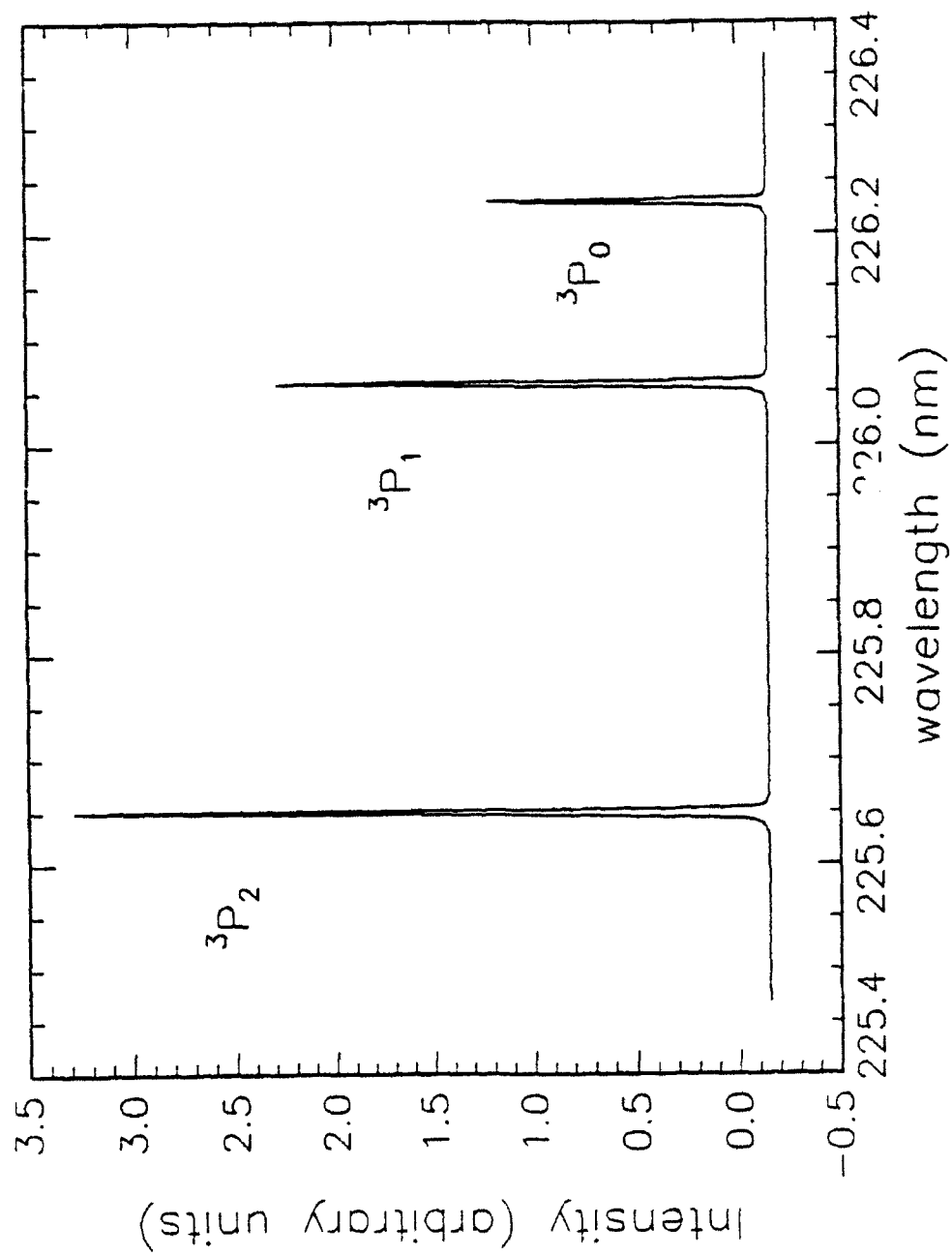


Figure 4 The 2 + 1 resonance enhanced multiphoton ionization spectrum of atomic oxygen.

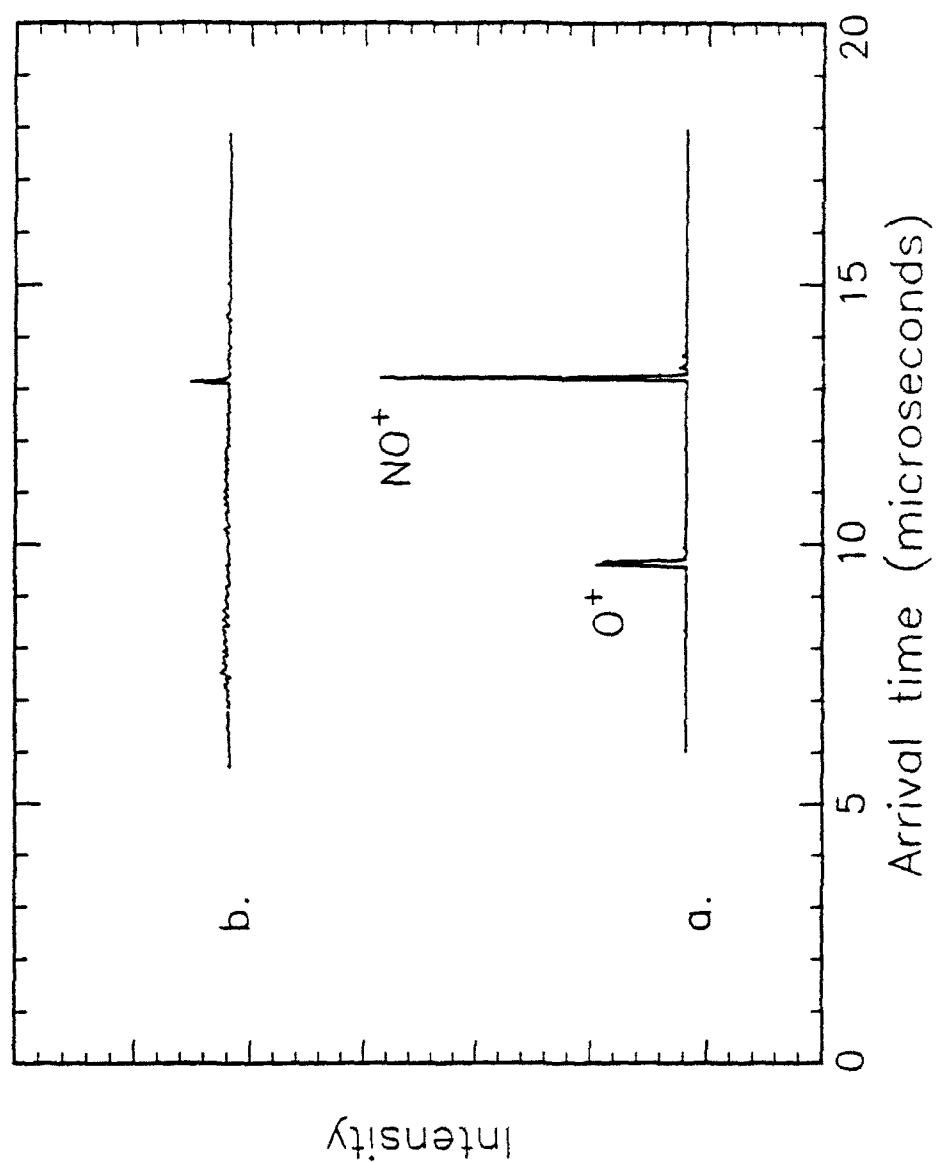


Figure 5 Comparison of TOF spectra; a. MPI of gas phase NO_2 ,
b. MPI probe of neutral ESD products from oxidized Ag.

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R. Ai	PhD 1992
M. I. Buckett	PhD 1991
G. Jayaram	
M. Jacobi	PhD 1993

Appendix: List of Publications

In Refereed Journals

1. Diffusion During Electron Beam Induced Reduction of Tungsten Trioxide.
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Ultramicroscopy, 38, 325 (1991)
L. D. Marks
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L. D. Marks
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Ultramicroscopy, 45, 145 (1992)
P. Xu and L. D. Marks

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13. Problems with the use of Surfaces Reconstructions as
Indicators of a Well-Ordered Surface
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R. Ai, H.-J. Fan and L. D. Marks
15. Phase Transition Kinetics of Vanadium Pentoxide
II: Theoretical Results
Surface Science, 280, 375 (1993)
L. D. Marks, V. A. Volpert and R. Ai
16. Thermal Shock Cleavage of Silicon (111) Thin Film
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T. S. Savage, P. Xu and L. D. Marks
17. Atomic Imaging of Surfaces in Plane View
Surface Science Letters 285, L479 (1993)
P. Xu, D. Dunn, J. P. Zhang and L. D. Marks
18. UHV Microscopy of the Si (111) Boron $\sqrt{3}\times\sqrt{3}$ R30° Surface
Journal of Vacuum Science and Technology, in press
L. D. Marks, R. Ai, S. Savage and J. P. Zhang
19. Phase Transitions in Metal Oxides under Irradiation
Phase Transitions, in press
V. A. Volpert, L. D. Marks and R. Ai
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